

# PATENT ABSTRACTS OF JAPAN

(11)Publication number : 2004-349458

(43)Date of publication of application : 09.12.2004

(51)Int.CI. H01L 21/316  
H01L 21/31

(21)Application number : 2003-144613

(71)Applicant : OMI TADAHIRO  
TOKYO ELECTRON LTD

(22)Date of filing : 22.05.2003

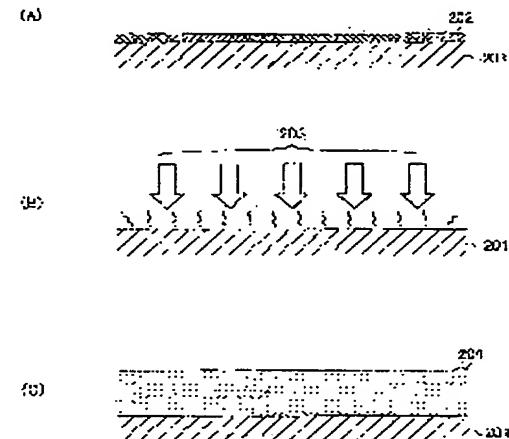
(72)Inventor : OMI TADAHIRO  
HIRAYAMA MASAKI

## (54) PROCESS FOR FORMING FLUORINE ADDED CARBON FILM

### (57)Abstract:

PROBLEM TO BE SOLVED: To provide a process for forming a fluorine added carbon film in which adhesion is enhanced between the fluorine added carbon film and an underlying film without causing any damage on the underlying film.

SOLUTION: The process for forming a fluorine added carbon film on a substrate to be processed comprises a first step for performing surface treatment of the substrate to be processed with rare gas subjected to plasma excitation by a substrate processing equipment, and a second step for forming a fluorine added carbon film on the substrate to be processed wherein the substrate processing equipment has a microwave antenna electrically connected with a microwave power supply.



### LEGAL STATUS

[Date of request for examination] 28.12.2005

[Date of sending the examiner's decision of rejection]

[Kind of final disposal of application other than the examiner's decision of rejection or application converted registration]

[Date of final disposal for application]

[Patent number]

[Date of registration]

[Number of appeal against examiner's decision of rejection]

[Date of requesting appeal against examiner's decision of rejection]

**BEST AVAILABLE COPY**

[Date of extinction of right]

Copyright (C); 1998,2003 Japan Patent Office

(19) 日本国特許庁(JP)

## (12) 公開特許公報(A)

(11) 特許出願公開番号

特開2004-349458

(P2004-349458A)

(43) 公開日 平成16年12月9日(2004.12.9)

(51) Int.Cl.<sup>7</sup>  
H01L 21/316  
H01L 21/31F 1  
H01L 21/316  
H01L 21/31M  
Cテーマコード(参考)  
5FO45  
5FO58

審査請求 未請求 請求項の数 12 O.L. (全 17 頁)

(21) 出願番号 特願2003-144613 (P2003-144613)  
(22) 出願日 平成15年5月22日 (2003.5.22)(71) 出願人 000205041  
大見 忠弘  
宮城県仙台市青葉区米ヶ袋2-1-17-  
301  
(71) 出願人 000219967  
東京エレクトロン株式会社  
東京都港区赤坂五丁目3番6号  
(74) 代理人 100070150  
弁理士 伊東 忠彦  
(72) 発明者 大見 忠弘  
宮城県仙台市青葉区米ヶ袋2-1-17-  
301  
(72) 発明者 平山 昌樹  
宮城県仙台市青葉区荒巻字青葉10 東北  
大学 未来科学技術共同研究センター内  
最終頁に続く

(54) 【発明の名称】フッ素添加カーボン膜の形成方法

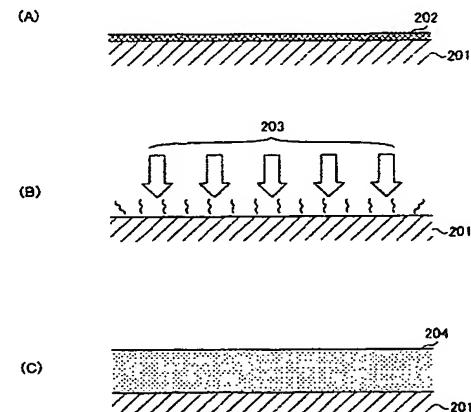
## (57) 【要約】

【課題】フッ素添加カーボン膜と下地膜との密着性を改善する

【解決手段】被処理基板上にフッ素添加カーボン膜を形成するフッ素添加カーボン膜の形成方法であって、基板処理装置によって希ガスをプラズマ励起し、プラズマ励起された前記希ガスによって前記被処理基板の表面処理を行う第1の工程と、前記被処理基板上にフッ素添加カーボン膜を形成する第2の工程を含み、前記基板処理装置は、マイクロ波電源が電気的に接続されたマイクロ波アンテナを有することを特徴とするフッ素添加カーボン膜の形成方法。

【選択図】

図2



\* NOTICES \*

JPO and NCIPI are not responsible for any damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. \*\*\*\* shows the word which can not be translated.
3. In the drawings, any words are not translated.

---

CLAIMS

---

[Claim(s)]

[Claim 1]

It is the formation approach of the fluoridation carbon film which forms the fluoridation carbon film on a processed substrate,  
The 1st process which carries out plasma excitation of the rare gas with a substrate processor, and performs surface treatment of said processed substrate with said rare gas by which plasma excitation was carried out,  
The 2nd process which forms the fluoridation carbon film on said processed substrate is included,

Said substrate processor,

The formation approach of the fluoridation carbon film characterized by to carry out plasma excitation of the plasma gas with which the microwave power source which has the microwave transparency aperture prepared so that said processed substrate might be met, and was established on said microwave transparency aperture introduces microwave into the process space on said processed substrate through said microwave aperture, and contains said rare gas from the microwave antenna connected electrically.

[Claim 2]

The formation approach of the fluoridation carbon film according to claim 1 characterized by forming the fluoridation carbon film at said 2nd process on said processed substrate with which said surface preparation was performed in said 1st process.

[Claim 3]

Said substrate processor,

The processing container equipped with the maintenance base which is formed with an outer wall and holds said processed substrate,

It has the exhaust port which exhausts said processing container,

Said microwave transparency aperture is the formation approach of the fluoridation carbon film according to claim 1 or 2 characterized by being installed on said processing container, inserting the plasma gas feed zone which supplies said plasma gas between said processing container and said microwave transparency aperture, and forming said some of outer walls.

[Claim 4]

Said microwave antenna is the formation approach of the fluoridation carbon film given [ among claims 1-3 for which electric power was supplied by the coaxial waveguide and which were characterized by consisting of a dielectric prepared between the body of an antenna which has opening, the microwave radiation side which has two or more slots established so that said opening might be covered on said body of an antenna, and said body of an antenna and said microwave radiation side ] in any 1 term.

[Claim 5]

Said rare gas is the formation approach of the fluoridation carbon film given [ among claims 1–4 characterized by including Ar ] in any 1 term.

[Claim 6]

Said rare gas is the formation approach of the fluoridation carbon film given [ among claims 1–4 characterized by including Kr ] in any 1 term.

[Claim 7]

Said rare gas is the formation approach of the fluoridation carbon film given [ among claims 1–4 characterized by including Xe ] in any 1 term.

[Claim 8]

Said process space is the formation approach of the fluoridation carbon film given [ among claims 1–7 characterized by to be divided into the 1st space which faces said microwave transparency aperture with the electrical conducting material structure, and to include, and the 2nd space facing said processed substrate to include, to supply the raw gas used as the raw material which forms the fluoridation carbon film in said 2nd space, and to perform said 2nd process with said substrate processor ] in any 1 term.

[Claim 9]

Said electrical conducting material structure is the formation approach of the fluoridation carbon film according to claim 8 characterized by being the raw gas feed zone which supplies said raw gas to said 2nd space.

[Claim 10]

Said raw gas feed zone is the formation approach of the fluoridation carbon film according to claim 9 characterized by having two or more openings which pass the plasma formed in said processing container, a raw gas path, and two or more raw gas supply holes which were open for free passage in said processing container from said raw gas path.

[Claim 11]

Said the 1st process and said 2nd process are the formation approach of the fluoridation carbon film given [ among claims 8–10 characterized by being carried out continuously in said substrate processor ] in any 1 term.

[Claim 12]

It is the formation approach of the fluoridation carbon film according to claim 11 which said 2nd process is performed after said 1st process, and is characterized by carrying out said 1st process where supply of said raw gas of said substrate processor is intercepted.

---

[Translation done.]

\* NOTICES \*

JPO and NCIPI are not responsible for any damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.
- 2.\*\*\*\* shows the word which can not be translated.
3. In the drawings, any words are not translated.

---

## DETAILED DESCRIPTION

---

### [Detailed Description of the Invention]

[0001]

#### [Field of the Invention]

Main-name invention relates to the formation approach of an insulator layer, especially relates to the formation approach of the fluoridation carbon film.

[0002]

#### [Description of the Prior Art]

To reduce the stray capacity during wiring of a semiconductor device, and to accelerate the working speed of a semiconductor device with high-performance-izing of a semiconductor device in recent years, is tried. In order to reduce the stray capacity during wiring, the method of using an ingredient with a low dielectric constant for the interlayer insulation film formed between wiring of a semiconductor device is taken.

[0003]

Although the silicon oxide (SiO<sub>2</sub> film) whose specific inductive capacity is about four has been used for the above mentioned interlayer insulation film, it is using the fluoridation silicon oxide (SiOF film) whose specific inductive capacity's is three to about 3.5, and improvement in the speed of a semiconductor device has been attained in recent years.

[0004]

However, it was difficult for a limitation to be to reduce specific inductive capacity by the above mentioned SiOF film, and to attain three or less specific inductive capacity.

[0005]

Although there are various candidate ingredients in the so-called low dielectric constant interlayer insulation film with low specific inductive capacity, specific inductive capacity is low and it is a requirement to have the mechanical strength which can bear for using for a semiconductor device. Then, its attention was paid to the fluoridation carbon film (CF film) which it has sufficient mechanical strength and can be made about 2.5 and less than [ it ] by specific inductive capacity, and the attempt which presupposes that it is a next-generation low dielectric constant interlayer insulation film, and is used for a semiconductor device has been performed.

[0006]

#### [Patent reference 1]

WO 99/No. 35684 official report

[0007]

#### [Problem(s) to be Solved by the Invention]

However, when the above mentioned fluoridation carbon film was used as an interlayer insulation film of a semiconductor device, there was a problem that the

adhesion force with the substrate of the fluoridation carbon film and the fluoridation carbon film concerned was weak.

[0008]

Drawing 1 (A) The example in the case of forming the fluoridation carbon film on a silicon nitride (SiN film) is shown in – (C). When using the fluoridation carbon film as an interlayer insulation film of a semiconductor device, the fluoridation carbon film is formed in many cases on the SiN film which is the cap layer of Cu layer which is a wiring layer of the semiconductor device concerned.

[0009]

With reference to drawing 1 (A), SiN film 101 is formed on the processed substrate which is not illustrated. Moreover, on said SiN film 101, compared with said SiN film 101, it is dramatically thin, for example, the adhesion layer 102 which consists of moisture, the organic substance, natural oxidation film, etc. is formed. After said SiN film 101 is formed, said adhesion layer 102 will put a processed substrate to atmospheric air, and will be formed in many cases.

[0010]

next, drawing 1 (B) -- setting -- for example, plasma CVD (chemical vapor deposition) -- the fluoridation carbon film 103 is formed by law etc.

[0011]

However, since the adhesion layer 102 exists on SiN film 101 as described above, as shown in drawing 1 (C), said fluoridation carbon film 103 exfoliates from said SiN film 101 with said adhesion layer 102, or the case where said fluoridation carbon film 103 exfoliates from said adhesion layer 102 arises.

[0012]

Moreover, even when exfoliation which was described above did not arise immediately after formation of said fluoridation carbon film 103, it was difficult to secure sufficient adhesion force of the substrate film and fluoridation carbon film which the fluoridation carbon film may exfoliate in the production process of a semiconductor device in the heat treatment process which requires thermal stress, the process of CMP (chemical machinery polish) by which shearing stress etc. is applied further, and are satisfied with it of such a demand, for example.

[0013]

Moreover, in order to secure the adhesion force, when removing said adhesion layer 102, there is the approach of removing by the sputter etching by plasma treatment equipment. However, there was a problem that said SiN film 101 used as the substrate film of the fluoridation carbon film will receive a damage by the ion bombardment of sputter etching.

[0014]

So, it aims at offering the formation approach of the fluoridation carbon film which solved the above-mentioned technical problem in this invention.

[0015]

The concrete technical problem of main-name invention is offering the formation approach of the fluoridation carbon film which makes good the adhesion force of the fluoridation carbon film and said substrate film, without giving a damage to the substrate film of the fluoridation carbon film.

[0016]

[Means for Solving the Problem]

In order that this invention may solve the above-mentioned technical problem, It indicated to claim 1,

It is the formation approach of the fluoridation carbon film which forms the fluoridation carbon film on a processed substrate,

The 1st process which carries out plasma excitation of the rare gas with a substrate

processor, and performs surface treatment of said processed substrate with said rare gas by which plasma excitation was carried out,  
The 2nd process which forms the fluoridation carbon film on said processed substrate is included,  
Said substrate processor,  
the formation approach of the fluoridation carbon film characterized by to carry out the plasma excitation of the plasma gas with which the microwave power source which has the microwave transparency aperture prepared so that said processed substrate might be met, and was established on said microwave transparency aperture introduces microwave into the process space on said processed substrate through said microwave aperture, and contains said rare gas from the microwave antenna connected electrically -- moreover  
It indicated to claim 2,  
the formation approach of the fluoridation carbon film according to claim 1 characterized by forming the fluoridation carbon film at said 2nd process on said processed substrate with which said surface preparation was performed in said 1st process -- moreover  
It indicated to claim 3,  
Said substrate processor,  
The processing container equipped with the maintenance base which is formed with an outer wall and holds said processed substrate,  
It has the exhaust port which exhausts said processing container,  
the formation approach of the fluoridation carbon film according to claim 1 or 2 characterized by being installed on said processing container, inserting the plasma gas feed zone which supplies said plasma gas between said processing container and said microwave transparency aperture, and said microwave transparency aperture forming said some of outer walls -- moreover  
It indicated to claim 4,  
said body [ for which electric power is supplied to said microwave antenna by the coaxial waveguide / which has opening ] of antenna, and body top of an antenna -- said opening -- a wrap -- the formation approach of the fluoridation carbon film given [ among claims 1-3 characterized by consisting of a dielectric prepared between the microwave radiation side which has two or more slots established like, and said body of an antenna and said microwave radiation side ] in any 1 term -- moreover  
It indicated to claim 5,  
the formation approach of the fluoridation carbon film given [ among claims 1-4 characterized by said rare gas containing Ar ] in any 1 term -- moreover  
It indicated to claim 6,  
the formation approach of the fluoridation carbon film given [ among claims 1-4 characterized by said rare gas containing Kr ] in any 1 term -- moreover  
It indicated to claim 7,  
the formation approach of the fluoridation carbon film given [ among claims 1-4 characterized by said rare gas containing Xe ] in any 1 term -- moreover  
It indicated to claim 8,  
the formation approach of the fluoridation carbon film given [ among claims 1-7 characterized by for said process space to be divided into the 1st space which faces said microwave transparency aperture with the electrical conducting material structure, and to include, and the 2nd space facing said processed substrate, and for the raw gas used as the raw material which forms the fluoridation carbon film in said 2nd space to be supplied, and to be performed said 2nd process with said substrate processor ] in any 1 term -- moreover

It indicated to claim 9,

the formation approach of the fluoridation carbon film according to claim 8 characterized by said electrical conducting material structure being a raw gas feed zone which supplies said raw gas to said 2nd space -- moreover

It indicated to claim 10,

the formation approach of the fluoridation carbon film according to claim 9 characterized by equipping said raw gas feed zone with two or more openings which pass the plasma formed in said processing container, a raw gas path, and two or more raw gas supply holes which were open for free passage in said processing container from said raw gas path -- moreover

It indicated to claim 11,

the formation approach of the fluoridation carbon film given [ among claims 8-10 characterized by performing said the 1st process and said 2nd process continuously in said substrate processor ] in any 1 term -- moreover

It indicated to claim 12,

Said 2nd process is performed after said 1st process, and said 1st process is solved by the formation approach of the fluoridation carbon film according to claim 11 characterized by carrying out where supply of said raw gas of said substrate processor is intercepted.

### [Function]

According to this invention, plasma treatment equipment enables it to raise the adhesion force of the fluoridation carbon film and processed substrate front face which are formed after the surface preparation concerned by performing surface preparation of a processed substrate.

[0017]

Moreover, said plasma treatment equipment becomes possible [ performing said surface treatment ], without giving a damage to a processed substrate front face, since the microwave plasma of high density and low electron temperature is used.

[0018]

## [Embodiment of the Invention]

## [Principle]

First, the principle by which the adhesion force of the substrate film with which the fluoridation carbon film concerned is formed, and the fluoridation carbon film concerned is improved is explained by the formation approach of the fluoridation carbon film by this invention based on [drawing 2](#) (A) – (C).

[0019]

The fluoridation carbon film is used as an interlayer insulation film formed between the wiring layers of a semiconductor device, for example, it is formed in many cases on the silicon nitride (SiN film) which is the cap layer of Cu layer which is a wiring layer of a semiconductor device.

[0020]

First, with reference to drawing 2 (A), SiN film (silicon nitride) 201 used as the substrate film of the fluoridation carbon film is formed on the processed substrate which is not illustrated. On said SiN film 201, the adhesion layer 202 which consists of moisture, the organic substance, natural oxidation film, etc. is formed. said adhesion layer 202 -- typical -- about 0.1-1nm -- it is a film very much.

[0021]

Said adhesion layer 202 will be formed in many cases, if said SiN film 202 is put to the atmospheric air in which moisture and the organic substance exist. Usually, since the equipment which forms said SiN film 201 differs from the equipment which forms the fluoridation carbon film on said SiN film 201 and there is the need of conveying [ be / it / under / atmospheric-air / minding ] the processed substrate with which

said SiN film 201 was formed, it is dramatically difficult to prevent formation of an adhesion layer which was described above.

[0022]

So, in this invention, as shown in drawing 2 (B), the reaction kinds 203 which carried out microwave plasma excitation of the rare gas, such as ion and a radical, perform surface treatment of the substrate film from which said adhesion layer 202 on said SiN film 201 is removed. Moreover, if the electron temperature of the plasma is high in that case and the energy of the ion in said reaction kind is high, the energy to which ion collides with said SiN film 201 may become large, and a damage may be given to said SiN film 201. Therefore, it is required not to give a damage to said SiN film 201 which is substrate film, and to remove said adhesion layer 202, and it is possible in this invention to process by the microwave plasma which serves as a low electron temperature with the plasma treatment equipment using the microwave plasma mentioned later, and to process, without giving a damage to said SiN film 201.

[0023]

After removing said adhesion layer 202 at the process of drawing 2 (B), as shown in drawing 2 (C), the fluoridation carbon film 204 is formed. Since the adhesion layer 202 which becomes the cause of reducing the adhesion force of said SiN film 201 and said fluoridation carbon film 204, in the process of drawing 2 (B) is removed as described above, said SiN film 201 and said fluoridation carbon film 204 become possible [ holding the good adhesion force ].

[0024]

Next, the gestalt of operation of this invention is explained based on a drawing.

[The 1st example]

The flow chart of the formation approach of the fluoridation carbon film by the 1st example of this invention is shown in drawing 3. If processing is first started by the fluoridation carbon film formation approach by this invention with reference to drawing 3 in step 100 (it is the same as that of 100, a notation, and the following among [ S ] drawing), in step 200, as described above, surface treatment of the substrate film of the fluoridation carbon film formed in the processed substrate will be performed, and the adhesion layer formed in the front face of the substrate film will be removed.

[0025]

Next, in step 300, the fluoridation carbon film is formed on the substrate film from which the adhesion layer was removed, and processing is ended at step 400.

[0026]

As described above, by the formation approach of the fluoridation carbon film of this invention, it divides roughly and consists of surface down stream processing P which removes the adhesion layer of the front face of the substrate film, and a membrane formation process D which forms the fluoridation carbon film.

[0027]

Next, the plasma treatment equipment which carries out said surface treatment process P and said membrane formation process D is explained.

## [The 2nd example]

First, the plasma treatment equipment 10 which performs said surface treatment process P and said membrane formation process D is explained based on drawing 4 (A), (B), and drawing 5 .

[0028]

First, with reference to drawing 4 (A), said plasma treatment equipment 10 is formed in the processing container 11 and said processing container 11, and has the maintenance base 13 which consists of AlN or aluminum 2O3 which holds the processed substrate 12 by the electrostatic chuck, and which was preferably formed of the isotropic pressure inflatable flexible bag technique (HIP) between heat.

[0029]

The inside of said processing container 11 is divided into space 11C formed of the approximately cylindrical internal dividing wall 15 between the space of the core near the core of said maintenance base 13, and said internal dividing wall 15 and said processing container. Moreover, the space of the above mentioned core is divided roughly into space 11A which separates the raw gas supply structure 24 concerned to space 11B and said space 11B of the side near said maintenance base 13, and counters them by gas-passageway 24A of the shape of a grid of the raw gas supply structure 24 mentioned later.

[0030]

Like, to the processed substrate 12 on regular intervals 13, i.e., said maintenance base, said space 11A, 11B, and 11C which forms the inside of said processing container 11 minds exhaust port 11D surrounding said maintenance base 13 preferably formed in three or more places at least two places by \*\*\*\* symmetric relation, and is exhausted and decompressed by exhaust air means, such as a vacuum pump.

[0031]

Said processing container 11 consists of an austenitic stainless steel which contains aluminum preferably, and the protective coat which consists of an aluminum oxide by oxidation treatment is formed in the internal surface. Moreover, the microwave transparency aperture 17 which penetrates microwave is installed in the part corresponding to said processed substrate 12 among the outer walls of said processing container 11, and between said microwave transparency apertures 17 and said processing containers 11, the plasma gas installation ring 14 which introduces plasma gas is inserted, and the outer wall of said processing container 11 is formed, respectively.

[0032]

Said microwave transparency aperture 17 has a level difference configuration in the periphery section, engages with the level difference configuration in which the level difference configuration section concerned was prepared in said plasma gas installation ring 14, and has the structure where the airtight in said processing space 11 is further held by seal ring 16A.

[0033]

Plasma gas is introduced into said plasma gas installation ring from plasma gas inlet 14A, and the inside of gas slot 14B formed in abbreviation annular is diffused. The plasma gas in said gas slot 14B is supplied to said space 11A through plasma gas supply hole 15B formed in said internal dividing wall 15 further attached in said plasma gas installation ring 14 from two or more plasma gas hole 14C which is open for free passage to said gas slot 14B.

[0034]

It is possible for said internal dividing wall 15 to consist of an approximately cylindrical conductor, for example, a stainless alloy, and for heater 15B to be installed in the field which counters the outside of said internal dividing wall 15, i.e., the outer wall of said processing container 11, and to heat said internal dividing wall 15. Furthermore, said internal dividing wall 15 has structure which is electrically connected to said plasma gas installation ring 14, and is grounded through the plasma gas installation ring 14 concerned.

[0035]

Moreover, said microwave transparency aperture 17 consists of precise aluminum 2O3 formed by the HIP method. The microwave transparency aperture 17 of aluminum 2O3 formed by this HIP method is formed using Y2O3 as sintering acid, and although it is less than AlN to which porosity reaches 30W/m and K excluding pore or a pinhole

substantially at 0.03% or less, it has the very big thermal conductivity as a ceramic.  
[0036]

The slot plate 18 of the shape of a disk which had many slots 18a and 18b which are close to said microwave transparency aperture 17, and are shown in drawing 4 (B) formed on said microwave transparency aperture 17, The body 22 of an antenna of the shape of a disk holding said slot plate 18, The radial line slot antenna 30 constituted with the late phase plate 19 which consists of low loss dielectric materials of aluminum2O3 pinched between said slot plates 18 and said bodies 22 of an antenna, SiO2, or Si3N4 is formed.

[0037]

It is equipped with said radial slot line antenna 30 through said plasma gas installation ring 14 on said processing container 11, and the microwave whose frequency is 2.45GHz or 8.3GHz is supplied to said radial line slot antenna 30 from the external source of microwave (not shown) through the coaxial waveguide 21.

[0038]

The supplied microwave is emitted into said processing container 11 through said microwave transparency aperture 17 from the slots 18a and 18b on said slot plate 18, and excites the plasma in space 11A of said microwave transparency aperture 17 directly under in the plasma gas supplied from said plasma gas supply hole 15A. The excited plasma has structure which can measure the spectrum of observation or luminescence etc. from the measurement aperture 25 which was prepared in said processing container 11 and which consists of a quartz, sapphire, etc., for example.

[0039]

In order that it may be sealed by seal ring 16B between said radial line slot antenna 30 and said plasma gas installation ring and it may raise the adhesion of said radial line slot antenna 30 and said microwave transparency aperture 17, it becomes possible to push said radial line slot antenna 30 against said microwave transparency aperture 17 firmly with an atmospheric pressure by decompressing the clearance formed between said slot plate 18 and said microwave transparency aperture 17 with a vacuum pump (not shown).

[0040]

Outside waveguide 21A is connected to the body 22 of an antenna of the shape of said disk among said coaxial waveguide 21A, and central conductor 21B is connected to said slot plate 18 through opening formed in said slow wave plate 19. Then, the microwave supplied to said coaxial waveguide 21A is emitted from said slots 18a and 18b, going on between said bodies 22 of an antenna and slot plates 18 in the direction of a path.

[0041]

Drawing 4 (B) shows the slots 18a and 18b formed on said slot plate 18.

[0042]

With reference to drawing 4 (B), said slot 18a is arranged by concentric circular, and, similarly slot 18b which goes to this direct is formed in concentric circular corresponding to each slot 18a. Said slots 18a and 18b are formed at spacing corresponding to the wavelength of the microwave of said slot plate 18 radially compressed with said late phase plate 19, and as a result, microwave turns into an approximate plane wave from said slot plate 18, and is emitted. Since said slots 18a and 18b are formed by the relation relation and mutual cross at right angles in that case, the microwave emitted by doing in this way forms the circularly-polarized wave containing two polarization components which intersect perpendicularly.

[0043]

Furthermore with the plasma treatment equipment 10 of drawing 4 (A), the cooling block 20 which had cooling water path 20A formed is formed on said body 22 of an

antenna, and the heat accumulated in said microwave transparency aperture 17 is absorbed through said radial line slot antenna 30 by cooling said cooling block 20 with the cooling water in said cooling water path 20A. It lets the cooling water which said cooling water path 20A is formed in the shape of a spiral on said cooling block 20, and eliminated dissolved oxygen by carrying out bubbling of the H<sub>2</sub> gas preferably, and controlled the oxidation reduction potential pass.

[0044]

Moreover, with the plasma treatment equipment 10 of drawing 4 (A), among said processing container 11, it consists of a conductor between said microwave transparency apertures 17 and processed substrates 12 on said maintenance base 13, and the raw gas supply structure 24 installed so that it might be supported by the raw gas installation way 23 and might stand up is installed in it. It has the structure where raw gas is introduced into said raw gas installation way 23 from the raw gas inlet (not shown) established in the outer wall of said processing container 11.

[0045]

Said raw gas supply structure 24 has raw gas path 24A of the shape of a grid which is open for free passage on the raw gas installation way 23, from raw gas supply hole 24B of a large number which are further open for free passage from said raw gas path 24A to said space 11B, raw gas is supplied to said space 11B, and desired uniform substrate processing is made in said space 11B.

[0046]

Drawing 5 is the bottom view showing the configuration of the raw gas supply structure 24 of drawing 4 (A).

[0047]

With reference to drawing 5, it consists of conductors containing Mg, such as aluminum alloy and aluminum addition stainless steel, and it connects with said raw gas installation way 23, raw gas is supplied to said grid-like raw gas path 24A, and said raw gas supply structure 24 emits raw gas to homogeneity at said space 11B from said raw gas supply hole 24B of a large number by which underside formation was carried out. Moreover, said raw gas installation way 23 consists of a conductor, and said raw gas feeder style 24 has structure which is electrically connected to said raw gas installation way 23, and is grounded through the raw gas installation way 23 concerned.

[0048]

Moreover, opening 24C which passes the plasma and gas is formed between raw gas path 24A which adjoins said raw gas supply structure 24. When forming said raw gas supply structure 24 with a Mg content aluminum alloy, it is desirable to form the fluoride film in a front face. Moreover, when forming said raw gas supply structure 24 by aluminum addition stainless steel, it is desirable to form the passive state film of an aluminum oxide in a front face. With the plasma treatment equipment 10 by this invention, since the electron temperature in the plasma excited is low, the incidence energy of the plasma is small, and the problem which sputtering of this raw gas supply structure 24 is carried out, and metal contamination produces in the processed substrate 12 is avoided.

[0049]

Raw gas path 24A of the shape of said grid and raw gas supply hole 24B are prepared so that a little larger field than the processed substrate 12 shown in drawing 5 with the broken line may be covered. By establishing this raw gas supply structure 24 between said microwave transparency apertures 17 and processed substrates 12, plasma excitation of said raw gas is carried out, and this raw gas by which plasma excitation was carried out enables it to process to homogeneity.

[0050]

In forming said raw gas supply structure 24 with conductors, such as a metal, said raw gas supply structure 24 forms the short circuit side of microwave by setting up shorter than the wavelength of said microwave said spacing between grid-like raw gas path 24A.

[0051]

In this case, the microwave excitation of the plasma is produced in said space 11A, and raw gas is activated by the plasma diffused from said excitation space 11A in space 11B including the front face of said processed substrate 12. Moreover, since it can prevent putting said processed substrate 12 to direct microwave at the time of plasma firing, breakage on the substrate by microwave can also be prevented.

[0052]

Since supply of raw gas is uniformly controlled by the plasma treatment equipment 10 by this example by using the raw gas supply structure 24, even when the problem of superfluous dissociation in processed substrate 12 front face of raw gas can be solved and the large structure of an aspect ratio is formed in the front face of the processed substrate 12, it is possible to carry out desired substrate processing even in the inner part of this high aspect structure. That is, plasma treatment equipment 10 is effective in manufacture of many generations' semiconductor device with which design rules differ.

[The 3rd example]

Next, the formation approach of the concrete fluoridation carbon film using said plasma equipment 10 is shown in the flow chart of drawing 6. Drawing 6 shows concretely the formation approach of the fluoridation carbon film shown in drawing 2 (A) – (C) and drawing 3.

[0053]

With reference to drawing 6, the formation approach of the fluoridation carbon film by this invention consists of a membrane formation process D which forms the fluoridation carbon film on the processed substrate front face after the surface-preparation process P of a processed substrate, and surface preparation, as described above.

[0054]

First, if processing is started at step 500, in step 510, 400sccm installation of the Ar gas will be carried out from said plasma gas supply ring 14 as the 1st plasma gas.

[0055]

Next, in step 520, from said radial line slot antenna 30, microwave is introduced in said processing container 11 through said microwave installation aperture 17, and the microwave plasma is excited. In that case, since said radial line slot antenna 30 is used for microwave, it turns into an approximate plane wave from said slot plate 18, is emitted, and it becomes possible [ exciting the plasma with a low electron temperature ] with high density in order to form the circularly-polarized wave containing two more polarization components which go direct.

[0056]

Therefore, in step 530, the reaction kind containing Ar ion required for substrate surface treatment is fully generated, and it becomes possible to mainly remove said adhesion layer 202 on said SiN layer 201 by sputtering by Ar ion. Since the energy with which the Ar ion concerned collides with said SiN film 201 since electron temperature is still lower is stopped low, a damage is not given to said SiN film 201. In this way, in order not to give a damage to the substrate film of fluoridation carbon film, such as an SiN film, the plasma of a low electron temperature from which the energy of ion is set to about 6eV or less is needed.

[0057]

In this step, it becomes possible to remove said adhesion layers 202, such as

moisture on SiN film 201 concerned, and the organic substance, natural oxidation film, without giving a damage to said SiN film 201 by performing processing for 20 seconds by microwave power 1800W, Ar flow rate 400sccm, and the pressure of 133Pa (1Torr). The energy of Ar ion in this case is 5.6eV, and does not give a damage to an SiN film.

[0058]

Next, plasma gas supply is suspended with microwave installation at step 540, and the surface treatment process P is ended.

[0059]

Next, the membrane formation process D which forms the fluoridation carbon film on said SiN film 201 which ended surface preparation and became clarification is started.

[0060]

If the membrane formation process D is started in step 550, Ar and H<sub>2</sub> will be first introduced in said processing container 11 as the 2nd plasma gas from 600sccm(s), 40sccm, and said plasma gas supply ring 14, respectively.

[0061]

Next, microwave is introduced at step 560, as described above to said step 520, after exciting the plasma, in step 570, from said raw gas supply structure 24, 30sccm installation of the gas of the fluorocarbon system which is raw gas, C<sub>4</sub>F<sub>8</sub> [ for example, ], is carried out, and membrane formation of the fluoridation carbon film is started.

[0062]

At step 580, the with a dielectric constant of about 2.1 fluoridation carbon film 204 is formed on said SiN film 201 by membrane formation rate 340 nm/min by performing membrane formation processing in Ar flow rate 600sccm, H<sub>2</sub> flow-rate 40sccm, C<sub>4</sub>F<sub>8</sub> flow-rate 30sccm, and microwave power 2000W. In that case, as described above, it becomes possible by using the microwave plasma of high density and low electron temperature to form the good fluoridation carbon film of membranous quality with a low dielectric constant.

[0063]

Next, installation of plasma gas, raw gas, and microwave is suspended at step 590, and processing is ended at step 600.

[0064]

Since said adhesion layer 202 is removed from on said SiN film 201 used as the substrate film with which the fluoridation carbon film is formed as described above, the adhesion of the fluoridation carbon film 204 formed in step 590 and said SiN film 201 becomes good, and as further described above, there is no effect of a damage in the substrate of the fluoridation carbon film.

[0065]

For the aforementioned reason, the fluoridation carbon film formed by the formation approach of the fluoridation carbon film by this invention secures the adhesion force in which the heat treatment process and CMP process in a production process of a semiconductor device can be borne, and becomes possible [ using for a semiconductor device as a low dielectric constant interlayer insulation film ].

[0066]

Moreover, in this invention, although Ar is introduced at said step 510, when plasma excitation is carried out, Kr and Xe which can suppress the energy of ion low further may be used. For example, it is possible to hold down to 2.9eV in the case where ion energy uses 3.9eV and Xe in this example when [ of Ar ] Kr is used for replacing, and it is still more effective in stopping the damage to an SiN film.

[0067]

Moreover, the substrate film by which adhesion with the fluoridation carbon film is improved by this invention is not restricted to an SiN film (silicon nitride). As substrate film, for example, Si, SiO<sub>2</sub>, SiON, SiOC, SiCO (H), Insulator layers, such as an insulator layer (SOD film) formed with W, WN, Ta, TaN, Ti, TiN, Cu, aluminum, and other spin coat methods. It is possible to raise the adhesion force of the fluoridation carbon film and the substrate film, without receiving a damage in the substrate film like this example using a metal membrane, a metal nitride, a metal oxide film, etc., when forming the fluoridation carbon film on the substrate film concerned.

[The 4th example]

Moreover, as shown in drawing 7 below, even if it changes the formation approach of the fluoridation carbon film shown in drawing 6, it does so the same effectiveness as the case where it is shown in the 3rd example.

[0068]

Drawing 7 is a flow chart which shows the formation approach of the 4th example fluoridation carbon film of this invention. However, the same reference mark is given to the part explained previously among drawing, and explanation is omitted.

[0069]

Steps 500-530 and steps 570-600 of this example are the same as that of the case where it is shown in drawing 6.

[0070]

In this example, plasma gas is changed in step 560A. In the front step 530, since this is membrane formation processing of the following fluoridation carbon film after the surface preparation which removes said adhesion layer 202 is completed, it shows that processing changed from said 1st plasma gas to said 2nd plasma gas is performed.

[0071]

From the condition which was carrying out 400sccm supply of the Ar as the 1st plasma gas in the front step 530, H<sub>2</sub> is introduced with Ar as the 2nd plasma gas, and, specifically, the flow rate of Ar and H<sub>2</sub> is set to 600sccm and 40sccm, respectively. Then, it has shifted to membrane formation of the fluoridation carbon film continuously.

[0072]

Thus, it becomes it is possible to shift to the membrane formation process D from the surface treatment process P, and possible continuously by changing gas, with the plasma excited to shorten the substrate processing time and to form the fluoridation carbon film efficiently.

[0073]

Also in this example, it becomes possible to form the substrate film concerned and the fluoridation carbon film with the good adhesion force, without giving a damage to the substrate film of the fluoridation carbon film.

[The 5th example]

Next, the result whose adhesion force of the substrate film and the fluoridation carbon film improved is explained below by the formation approach of the fluoridation carbon film by this invention.

[0074]

First, the measuring method of the adhesion force of the fluoridation carbon film is shown in drawing 8. However, the same reference mark is given to the part explained previously among drawing, and explanation is omitted. For example, when measuring the adhesion force of the fluoridation carbon film formed on the SiN film on a processed substrate described above to drawing 2 (C), as first shown in drawing 8, the test bar 205 is fixed with predetermined adhesives on said fluoridation carbon film 204. And the load when the load of the direction which separates from a processed

substrate is added to said test bar 205 where a processed substrate is fixed, and the fluoridation carbon film 204 exfoliates was made into the adhesion force.

[0075]

The measurement result of the adhesion force of the fluoridation carbon film and the substrate film measured with the adhesion force measuring method shown in drawing 8 is shown in drawing 9. When formed by the formation approach of the fluoridation carbon film by this invention shown in drawing 6, and when the process of steps 500-550 in drawing 6 was not performed, the experiment was conducted about the case where surface treatment of the substrate film is not performed, and compared those results.

[0076]

Moreover, the experiment was conducted, respectively about the case where the fluoridation carbon film is formed about said two kinds of cases on the SiN film formed on Si substrate, and the case where the direct fluoridation carbon film is formed on Si substrate.

[0077]

With reference to drawing 9, when forming the fluoridation carbon film on an SiN film, by performing surface preparation shown in steps 500-550 of drawing 6 in each case in the case of forming the direct fluoridation carbon film on Si substrate shows that the adhesion force of the fluoridation carbon film and a substrate is improved substantially.

[0078]

For example, when forming the fluoridation carbon film on an SiN film, and not performing surface treatment of an SiN film and surface treatment is performed to adhesion force being 32MPa(s), it turns out that the adhesion force is improving with 48MPa(s).

[0079]

This is considered for the adhesion force of the fluoridation carbon film and an SiN film to improve by removing the moisture on the substrate of the fluoridation carbon film, the organic substance, the natural oxidation film, etc., as described above.

[0080]

Moreover, it becomes possible to raise the adhesion force of the fluoridation carbon film and the substrate film of the substrate film, without the substrate film receiving a damage, also when an SiN film, the insulator layer of not only Si but others, an oxide film, a nitride, an acid nitride, a metal membrane, a metal oxide film, a metal nitride, etc. are used for the substrate film.

[0081]

As mentioned above, although this invention was explained about the desirable example, various deformation and modification are possible for this invention in the summary which it is not limited to the above-mentioned specific example, and was indicated to the claim.

[0082]

[Effect of the Invention]

According to this invention, plasma treatment equipment enabled it to raise the adhesion force of the fluoridation carbon film and processed substrate front face which are formed after the surface preparation concerned by performing surface preparation of a processed substrate.

[0083]

Moreover, said plasma treatment equipment became possible [ performing said surface treatment ], without giving a damage to a processed substrate front face, since the microwave plasma of high density and low electron temperature is used.

[Brief Description of the Drawings]

[Drawing 1] (A) – (C) is drawing having shown the condition that the fluoridation carbon film exfoliated.

[Drawing 2] (A) – (C) is drawing having shown the formation approach of the fluoridation carbon film by this invention in simulation.

[Drawing 3] It is the flow chart (the 1) which showed the formation approach of the fluoridation carbon film by this invention.

[Drawing 4] (A) and (B) are the schematic diagrams of the plasma treatment equipment which enforces the formation approach of the fluoridation carbon film by this invention.

[Drawing 5] It is the bottom view of raw gas supply structure used with the plasma treatment equipment of drawing 4.

[Drawing 6] It is the flow chart (the 2) which showed the formation approach of the fluoridation carbon film by this invention.

[Drawing 7] It is the flow chart (the 3) which showed the formation approach of the fluoridation carbon film by this invention.

[Drawing 8] It is drawing having shown the measuring method of the adhesion force of the fluoridation carbon film in simulation.

[Drawing 9] It is drawing having shown the measurement result of the adhesion force of the fluoridation carbon film.

#### [Description of Notations]

- 10 Plasma Treatment Equipment
- 11 Processing Container
- 11D Exhaust port
- 11A, 11B, 11C Space
- 12 Processed Substrate
- 13 Maintenance Base
- 14 Plasma Gas Installation Ring
- 14A Plasma gas inlet
- 14B Gas slot
- 14C Plasma gas hole
- 15 Internal Dividing Wall
- 15A Plasma gas supply hole
- 15B Heater
- 16A, 16B Seal ring
- 17 Microwave Transparency Aperture
- 18 Slot Plate
- 18a, 18b Slot
- 19 Late Phase Plate
- 20 Cooling Water Block
- 20A Cooling water path
- 21,110A Coaxial waveguide
- 21A Outside waveguide
- 21B Inside feeder
- 22,110B Body of an antenna
- 23 Raw Gas Installation Way
- 24 Raw Gas Supply Structure
- 24A Raw gas path
- 24B Raw gas training hole
- 24C Opening
- 25 Measurement Aperture
- 30 Radial Line Slot Antenna
- 101,201 Silicon nitride

102,202 Adhesion layer  
103,204 Fluoridation carbon film  
203 Reaction Kind

---

[Translation done.]

**This Page is Inserted by IFW Indexing and Scanning  
Operations and is not part of the Official Record**

**BEST AVAILABLE IMAGES**

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

**BLACK BORDERS**

**IMAGE CUT OFF AT TOP, BOTTOM OR SIDES**

**FADED TEXT OR DRAWING**

**BLURRED OR ILLEGIBLE TEXT OR DRAWING**

**SKEWED/SLANTED IMAGES**

**COLOR OR BLACK AND WHITE PHOTOGRAPHS**

**GRAY SCALE DOCUMENTS**

**LINES OR MARKS ON ORIGINAL DOCUMENT**

**REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY**

**OTHER:** \_\_\_\_\_

**IMAGES ARE BEST AVAILABLE COPY.**

**As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.**